EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Structural properties and in-depth chemical profile across the metal-insulator phase transition in V2O3 films under strain**	**Experiment number**: 25-02-956
Beamline:	**Date of experiment**: from: 18/11/2020 to: 21/11/2020 and from: 01/11/2021 to 05/11/2021	**Date of report**: 6 February 2022
Shifts:	**Local contact(s)**: Juan Rubio Zuazo and Jesús Lopez Sanchez	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): *Dr. Mariela Menghini *Dr. Alvaro Muñoz Noval *Dr. Oscar Rodriguez de la Fuente		

Report:

Abstract

Vanadium sesquioxide (V_2O_3) is a paradigmatic example of a Mott–Hubbard insulator in which a rich phase diagram results from the strong electron correlation and the competing degrees of freedom. The V_2O_3 system presents multiple phases that have dramatic differences in structural, electrical, optical and magnetic behavior. In bulk, undoped V_2O_3 undergoes a phase transition at a temperature of T_{MIT} ~160K from a paramagnetic metallic phase (PM) to an anti-ferromagnetic insulating one (AFI), characterized by an abrupt increase in resistivity of over 7 decades. This phase transition is accompanied by a structural one from a corundum structure to a monoclinic one. In thin films, the effect of substrate mismatch, interfaces and stoichiometry can play an important role in the structural and electronic phase transitions. For example, for ultra-thin films (thickness below 5 nm) the metal-insulator transition (MIT) is suppressed in strained films grown directly on Al_2O_3 substrates while the transition is preserved when using an almost lattice-matched buffer layer in between. Hence, it is of great importance to have a good understanding of how the local properties influence the macroscopic responses. The aim of the present proposal is to study the structural properties of pure V_2O_3 films across the MIT.

Experimental details and Results

Due to the COVID-19 situation this beamtime was split in two periods. The first one from 18/11/2020 till 21/11/2020 (9 shifts, remotely) and the second one from 01/11/2021 till 05/11/2021 (9 shifts, in person).

The samples studied during the two sessions of the experiments are:

Sample 0001 (37 nm V_2O_3 on Al_2O_3): Comprehensive series of L- and theta-scans at RT and at 80 K. Snapshots at specific H K L position as a function of temperature while warming up from 80 K to RT. X-ray reflectometry at RT. L- and theta- scans around different reflections ((1 0 10), (-2 4 6) and (0 1 8)) at T = 220 K, 160 K, 140 K, 120 K, 100 K, 80 K.

Sample 0003a (4nm V_2O_3 on Al_2O_3): various L- and theta-scans at RT.

Sample VO_14 (62nm V_2O_3 on 38nm Cr_2O_3 buffer layer on Al_2O_3): Snapshots of HKL = (-2 4 6) and (-1 2 9) while cooling down and warming up between RT and 80 K. L- and theta- scans around different reflections ((1 0 10), (-2 4 6) and (0 1 8)) at T = 220 K, 160 K, 140 K, 120 K, 100 K, 80 K.

Ultra-thin films: SM0006 (3 u.c. V_2O_3 on Al_2O_3), SM0007 (1 u.c. V_2O_3 on Al_2O_3), SM0011 (1 u.c. V_2O_3 on Cr_2O_3/ Al_2O_3), SM0012 (3 u.c. V_2O_3 on Cr_2O_3/ Al_2O_3).
L- and theta- scans around reflections (1 0 10) and (3 0 0) reflections at RT (SM0006, SM0007, SM0011) and at 80 K (SM0006, SM0012).

HAXPES experiments could not be performed as the substrates are highly insulating.

The reciprocal space maps constructed from the L- and theta-scans as a function of temperature in thick V_2O_3 films (Sample 0001 and VO_14) show the formation of three diffraction peaks in the ab-plane oriented at 120° from each other at temperatures around 160 K. These three lobes disappear when cooling further down to 100 K. At that same temperature, the diffraction peak in the c-direction (out-of-plane) splits into three peaks (see Fig. 1). This behavior has been observed in both samples (Sample 0001 and VO_14) with different thickness (37nm and 62nm) and grown on different surfaces (Al_2O_3 and Cr_2O_3/ Al_2O_3). This indicates that the observed structural evolution with temperature is an intrinsic property of the MIT in V_2O_3.
Preliminary analysis of the reciprocal space maps of 3 u.c. thick V_2O_3 films at RT and 80 K indicate that there is no structural phase transition when the film is grown directly on Al_2O_3 substrate. The RT high-angle diffraction shows that there is a reduction of the c-axis lattice parameter when reducing the thickness of the film from 3 u.c to 1 u.c..
Sample 0003a seem to be degraded, likely due to being exposed to air for too long time.

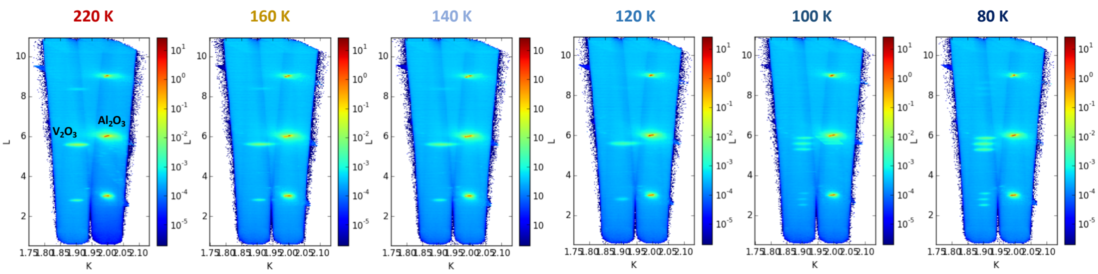

Figure 1. 22L scans as a function of temperature on 37 nm thick V_2O_3 film grown on Al_2O_3 substrate

Conclusions and future work
As mentioned in the abstract the MIT in V_2O_3 is accompanied by a structural transition from a corundum structure to a monoclinic one (PM to AFI transition). The observation of three preferential directions in the diffraction peaks when going through the MIT is rather unexpected. In similar V_2O_3 films, we have previously observed by means of PEEM (Photoemission electron microscopy) the formation of stripe domains in the AFI phase oriented at 120° with each other. These domains were associated with the three possible directions for the monoclinic distortion to take place. The in-depth analysis of the diffraction data collected in this beamtime will be crucial to understand the microscopic details of the structural phase transition and the relation with the striped nanostructured observed previously in V_2O_3 films. In the future, the growth of V_2O_3 films on less insulating substrates will be investigated. This could allow the study of structure and composition of the films with depth resolution as a function of temperature.
The preliminary analysis of the results on the ultra-thin samples indicate that the observed structural changes can be correlated to a metal-insulator transition due to quantum confinement when reducing the thickness to a single unit cell. Further diffraction studies along different crystalline orientations can be helpful to have a complete picture of the structural characteristics of this phase transition.
Due to technical problems at ESRF the beam was down for considerable time during our beamtime. Therefore, it was not possible to complete the set of measurements planned for this experiment.